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Thermal stability of titanium hydride thin films

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The thermal stability of titanium hydride thin films prepared by reactive evaporation is reported. The release of hydrogen is monitored by the effusion method. The gas evolution spectrum shows two peaks corresponding to the hydrogen effusion from the titanium hydride phase and to the crystallographic transformation from fcc to hcp structure, respectively.

Neutron supermirrors are multilayers of nickel and titanium. The reflectivity of this system can be still improved if pure titanium is replaced by titanium saturated with hydrogen, which would give an increased difference between the two indices of refraction and would allow one to diminish the number of layers needed.¹ It is then necessary to introduce hydrogen in titanium and to study its thermal stability.

This letter shows that it is possible to prepare hydrogenated titanium thin films by reactive evaporation. Their thermal stability is reported. The structure of the films is characterized by electron and x-ray diffraction. The release of hydrogen is monitored by the effusion method, a technique we used previously in the study of hydrogenated amorphous semiconductors.^{2,3}

Titanium was evaporated from an electron beam gun in a molecular hydrogen atmosphere onto substrates maintained at room temperature. The deposition rate ($1 \text{ \AA/s}$) was monitored and controlled with a quartz microbalance system. The hydrogen flow was regulated by maintaining the total pressure in the evaporation chamber at 10^{-4} Torr. Transmission electron microscopy was performed at room temperature on 200- $\text{\AA}$ -thick samples deposited on grids covered with carbon. X-ray diffraction and effusion experiments were carried out on 1000- $\text{\AA}$ -thick samples deposited on float glass substrates. X-ray measurements were performed with the K_{α} radiation of cobalt ($\lambda = 1.789 \text{ \AA}$). For gas evolution experiments, deuterated films were used to suppress background effects due to adsorbed water. Then, the films were inserted into a quartz tube evacuated by an ionic pump and were heated at a constant rate ($15 \text{ }^{\circ}\text{C/min}$) up to $750 \text{ }^{\circ}\text{C}$. The deuterium partial pressure was monitored by means of a quadrupole mass analyzer. At a constant pumping speed, it is directly proportional to the deuterium evolution rate. The D_2 partial pressure versus temperature was stored in a computer system to allow numerical analysis of the effusion spectra. Although D_2 was used in place of H_2 , the generic term hydrogen will be used in subsequent discussions.

A typical evolution spectrum, showing the hydrogen evolution rate, that is, the number of hydrogen atoms released per unit film volume per unit time against temperature, is represented in Fig. 1. Two peaks can be observed. The first peak has a low intensity and is very broad since it spreads between 200 and $400 \text{ }^{\circ}\text{C}$, then a second peak, intense and very narrow, appears at $405 \text{ }^{\circ}\text{C}$. In fact, if we take account of the areas of these peaks, the first contains about as much hydrogen as the second.

The electron and x-ray diffraction patterns of these films as prepared and annealed at 350 and $450 \text{ }^{\circ}\text{C}$ are represented in Figs. 2 and 3, respectively. The structure of the films as prepared and annealed at $350 \text{ }^{\circ}\text{C}$ is identified as the fcc CaF_2 structure of titanium hydride.⁴ In the x-ray pattern, the only intense peak is the (111) reflection, as expected from the Joint Committee for Powder Diffraction Standard file. Because of the small thickness of the sample, the other peaks are very weak. On the contrary, all the reflections expected for a fcc structure are observed in the electron diffraction pattern. The films annealed at $450 \text{ }^{\circ}\text{C}$ present the diffraction pattern of the titanium hcp phase.⁵ The x-ray pattern shows an intense (011) reflection with a lower (002) reflection. The (010) and (110) lines are hardly visible and the (012) line is absent. On the other hand, the electronic pattern again displays all the reflections expected for a hcp structure. This transformation from a TiH_2 structure to hcp Ti is due to the above-mentioned hydrogen effusion. This temperature is in agreement with the value obtained by Yanagida *et al.*,⁶ who observed the transformation of ultrafine particles of TiH_2 in titanium after a heat treatment at $400 \text{ }^{\circ}\text{C}$ for 1 min at a pressure of 10^{-6} Torr.

When titanium hydride films are heated, effusion occurs, which can be analyzed in terms of the three potential rate-limiting steps: detrapping of hydrogen from bound sites in the bulk, diffusion of hydrogen in the bulk solid, and desorption from the surface. In the case of titanium, the process is complicated by the structural change from a fcc hydrogen-rich TiH_2 phase to a hcp Ti phase with a low hydrogen solubility. It can therefore be thought that hydrogen contained in

FIG. 1. Thermal effusion spectrum of a titanium hydride thin film. The experimental points are represented by the symbol +. The dotted lines represent the simulated individual and total release rate curves.

FIG. 2. Electron diffraction patterns of a titanium hydride thin film as prepared or annealed at 350 °C (a) and annealed at 450 °C (b).

the hcp phase after the crystallographic transformation will exit very fast from this phase since its hydrogen solubility is low. This transformation corresponds to the second very narrow peak, which is comparable in width (20 °C) with crystallization peaks observed in thermal desorption⁷ or in differential scanning calorimetry experiments. The first peak, at lower temperatures, corresponds to the classical effusion phenomenon in the TiH₂ phase.

An easy way to determine whether the evolution rate is diffusion limited or not is the measurement of the thickness dependence. If diffusion limits the evolution rate, the rising diffusion length with increasing film thickness will result in a shift of the effusion peak to higher temperatures. Such a shift was not observed between films with thicknesses of 1000 and 3000 Å. Also, although it is difficult to precisely determine the rate-limiting step between detrapping from bound sites in the bulk and desorption from the surface, we tried to determine the kinetic parameters of the decomposition of TiH₂. The kinetics of the release of the dissolved hydrogen was analyzed using the Eyring theory of absolute rate processes.⁸ This theory assumes that the hydrogen atom must overcome a free energy barrier ΔG in order to be evolved and the frequency at which the barrier is confronted is approximated by the factor kT/h , where k and h are the Boltzmann and Planck constants, respectively, and T is the absolute temperature. Therefore, the effusion rate R follows the equation

$$R = \frac{d(c/c_0)}{dt} = \left(\frac{kT}{h}\right) \left(1 - \frac{c}{c_0}\right)^n \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right)$$

with c_0 and c the original and evolved hydrogen concentrations and n the order of the reaction. The free energy of desorption ΔG is equal to $\Delta H - T\Delta S$ where ΔH is the enthalpy and ΔS is the entropy of reaction. The experimental shape of the effusion curve determines the order n of the kinetics.

FIG. 3. X-ray diffraction patterns of a titanium hydride thin film as prepared (a) and annealed at 350 °C (b) and 450 °C (c).

Figure 1 shows the deconvoluted peaks and the total release rate, which is in the best agreement with the experimental curve. The fit was obtained with a second-order kinetics for the broad first peak and a first-order kinetics for the narrow second peak. The parameters of the fit are $\Delta H = 0.8$ eV and $\Delta S = -1.7 \times 10^{-3}$ eV K⁻¹ for the first peak and $\Delta H = 6.0$ eV and $\Delta S = 5.9 \times 10^{-3}$ eV K⁻¹ for the second peak, which corresponds to ΔG values of 1.8 and 2.0 eV, respectively.

In conclusion, we showed that the evaporation of titanium in a pressure $P_{H_2} = 10^{-4}$ Torr of molecular hydrogen allows one to obtain titanium hydride thin films with the fcc structure. Electron and x-ray diffraction indicate that titanium hydride transforms in the hcp titanium phase at 405 °C. Effusion experiments show that the release of hydrogen begins as soon as 200 °C. The effusion spectrum can be deconvoluted in two peaks. The first one is a low-intensity and broad peak with a maximum at 310 °C. It corresponds to the effusion from the titanium hydride phase with a ΔG value of 1.8 eV. The second one at 405 °C is an intense and narrow peak which corresponds to the crystallographic transformation with a ΔG value of 2.0 eV.

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⁵ JCPDS file No. 5-0682.

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